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OPALESCENT INK.

Merten Piel

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OPALESCENT INK

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Inventor:	Merten Piel
Applicant:	rotring international GmbH & Co KG

The invention concerns a water-based ink composition that contains a pearlescent pigment as colorant. In particular, the invention concerns an ink composition for writing implements such as fountain pens or tube filler pens.

The inks and printing inks known up to now that contain pearlescent pigments are not suitable for use in writing implements that have narrow outlet orifices, thin capillaries or tubes such as fountain pens and tube filler pens. For instance, an aqueous screen printing ink for printing on melamine resin plastics, which contains 25-50 wt% pearlescent pigment, binders and thickeners, is known from US-A-3 631 135. Such a screen printing ink is relatively viscous (about 100 mPa·sec) and, moreover, is a non-Newtonian liquid, so as to pass through the screen only by means of doctor knife pressure. In any case it is not suitable to be used for writing in fountain pens or tube filler pens. In addition, special pearlescent pigments and their use in printing inks are known from EP-A-0 321 739. However, the printing inks, like those mentioned

above, are too viscous to be used for writing with writing implements that have fine capillaries. Furthermore, inks with silver or gold effects are known for marker sticks. However, in many cases these contain high levels of organic solvents and pigments that contain elemental metal in order to produce the silver or gold effect. Because of the content of elemental metal one has to take into account corrosion problems if they are used in largely or exclusively aqueous media.

The task underlying the invention consists of making available an ink composition that can be applied to a writing surface from writing implements with narrow outlet orifices that produces an opalescent/iridescent color coat and is water based. At the same time the disadvantages that arise with the known inks and printing inks should be avoided.

The task in accordance with the invention is accomplished by a water-based ink composition that contains a pearlescent pigment as colorant and is characterized by the fact that it has a viscosity less than 12 mPa·sec (at 25°C) and contains 0.5-25 wt% pearlescent pigment, 55-95 wt% water and optionally other conventional additives.

Preferred embodiments are objects of the subordinate claims.

Surprisingly, the ink composition in accordance with the invention allows permanent writing, even though as a rule one assumes that pigments like the pearlescent pigments that are in use cannot be written from capillary ink passages over a long period of time because the capillaries will become plugged, and that pigments that settle rapidly like pearlescent pigments cannot lead to a uniform written line.

However, it turned out that even in the case of low viscosity inks, i.e., ones without the otherwise conventional stabilization of the pigments through high viscosity, thixotropic action, etc., not only is a uniform written line possible when such pigments are used, but sharp and very fine lines can be produced. The long-term writability of the pigments probably derives from the reversible flocculation capacity of the sediment that forms.

Different color tones that appear opalescent or iridescent result according to the angle of viewing of the color coatings that are produced. If desired, it is also possible to produce lines that have colors that are different in the middle than at the edges. This effect can be achieved, for example, by controlled adjustment of the spreading behavior, for example by means of the addition of surfactants.

The ink composition in accordance with the invention in general has a viscosity of less than 12 mPa·sec (at 25°C). Preferably, the viscosity is in the range from 1 to 10 mPa·sec (at 25°C) and especially preferably in the range from 1 to 5 mPa·sec (at 25°C).

The amount of pearlescent pigment in the ink composition is in general 0.5-25 wt%, preferably in the range from 1 to 20 wt% and especially in the range from 1 to 10 wt%, with a range from 1 to 5 wt% being particularly preferred. The water-based ink composition in accordance with the invention also in general contains 55-95 wt% water and preferably

75-90 wt% water, and 0.5-20 wt% water-miscible organic solvents may also be present. These solvents in particular are glycerol, ethanediol, propane-1,2-diol and ethanol.

The pearlescent pigment that is used in accordance with the invention can be metallic or nonmetallic, but preferably nonmetallic. Suitable pearlescent pigments consist of mica, coated with one or more metal oxides, or of pearl essence. Suitable metal oxides are, for example,  $\text{TiO}$ ,  $\text{TiO}_2$  or mixtures of these and  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  or mixtures of these, as well as  $\text{ZnO}$ . For example, the pearlescent pigment can consist of  $\text{TiO}_2$ -coated mica or mica coated with  $\text{TiO}_2$  and an iron oxide.

The pearlescent pigment is preferably in lamellar form and has an average diameter less than 60  $\mu\text{m}$  and preferably less than 20  $\mu\text{m}$ .

The ink composition can also contain other additives that are conventional for inks in addition to the pearlescent pigment and the water base. These include, for example, other pigments, water-soluble dyes, water-miscible organic solvents, dispersing agents, water-soluble binders, pH regulators, preservatives, surfactants and other additional auxiliary agents. Pigments other than the pearlescent pigments can be present in an amount from 0.5 to 10 wt%, the water-soluble dyes can be present in an amount from 0.1 to 10 wt%, the water-miscible organic solvents can be present in an amount from 0.5 to 2 wt%, the dispersion agents can be present in an amount from 0.1 to 5 wt%, the water-soluble binders can be present in an amount from 0.5 to 20 wt%, the pH regulators can be present in an amount from 0.1 to 2 wt%, the preservatives can be present in an amount from 0.01 to 0.5 wt%, the surfactants can be present in an amount from 0.001 to 5 wt%, and the additional auxiliary agents can be present in an amount from 0.1 to 10 wt%. Of these conventional additives one or several can be simultaneously present.

The additional pigments can be, for example, Pigment Black 7 or Pigment Blue 15:3. Suitable as water-soluble dyes are in particular Acid Blue 9, Acid Red 52, Acid Yellow 23 and Direct Black 19. Dispersion agents that may be used include, in particular, polyacrylates, and suitable binders are polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP). Citric acid and triethanolamine are possibilities as pH regulators, with citric acid being preferred. Potassium sorbate and p-chloro-m-cresol are preservatives that can be used in the ink composition in accordance with the invention. Compounds like polyglycol ether derivatives and lauryl ether sulfates are examples of usable surfactants. Urea is a possibility as another auxiliary agent.

The ink, because of its low viscosity, can be applied to the writing surface through narrow orifices, thin capillaries or small tubes. For this reason it can be used especially in writing implements like fountain pens or tube filler pens.

In order to achieve good and rapid distribution of the pigment particles in the ink during use, the ink can also include small inert mixing balls. The diameter of the mixing balls lies in the range from 0.5 to 3 mm, with a diameter of 0.8 mm being preferred. In practice such mixing

balls can be present, for example, in ink cartridges, with 1-3 mixing balls per ink cartridge being sufficient. The mixing balls consist of an inert material, preferably zirconium dioxide or glass. The deflocculation of the settled pearlescent pigment that has settled when the writing implement is resting (flocculation and formation of a soft sediment) is performed by the mixing balls on the basis of very light shearing such as by shaking a couple of times, and the pigment again becomes sufficiently finely distributed.

The described ink composition can be produced by mixing the individual components with each other in any order, where preferably one starts with the water which has been optionally slightly heated.

Examples of ink compositions in accordance with the invention are listed below.

#### Example 1

(Blue opalescent)

	wt%
Demineralized water	88.8
Iriodin 123*	3
Duasyn acid blue AE 85 (Acid Blue 9)	1
Glycerol	2
Urea	1
Citric acid	1
Potassium sorbate	0.1
Luviskol K30 (PVP) (Viscosity 10 mPa·sec (at 25°C) at 15°C in water [sic])	3
Nonylphenol polyglycol ether (95% ethylene oxide, Igepal CO 990 (surfactant)	0.1

\* Iriodin 123: Mica coated with TiO<sub>2</sub> and ZnO

Example 2

(Silvery, especially for black paper)

	wt%
Demineralized water	86.8
Iriodin 323*	5
Glycerol	2
Urea	1
Citric acid	1
Potassium sorbate	0.1
Luviskol K30 (PVP)	4
Igepal CO 990 (surfactant)	0.1

\* Iriodin 123: Mica coated with  $\text{TiO}_2$  and  $\text{ZnO}$ Example 3

(Gold ink)

	wt%
Demineralized water	87.8
Iriodin 323	4
Dye combination (gold-yellow)	1
Glycerol	2
Urea	1
Citric acid	1
Potassium sorbate	0.1
Luviskol K30 (PVP)	3
Igepal CO 990 (surfactant)	0.1

\* Iriodin 323: mica coated with  $\text{TiO}_2$  and iron oxide, gold-satin.

The "serum" (dissolved components) has the same color as the pearlescent pigment, so that a particularly intensive gold results.

A combination of 95 wt% brilliant black ink and 5 wt% Iriodin 110 (pearlescent pigment, mica coated with  $\text{TiO}_2$ ) can also be used. A silver gray ink results in this case.

Claims

1. A water-based ink composition that contains a pearlescent pigment as colorant, which is characterized by the fact that it has a viscosity less than 12 mPa·sec (at 25°C) and contains

0.5-25 wt% pearlescent pigment,  
55-95 wt% water and  
optionally other conventional additives.

2. An ink composition as in Claim 1, which is characterized by the fact that it has a viscosity in the range of 1-10 mPa·sec (at 25°C).

3. An ink composition as in Claim 1 or 2, which is characterized by the fact that it has a viscosity in the range of 1-5 mPa·sec (at 25°C).

4. An ink composition as in one of Claims 1-3, which is characterized by the fact that it contains 1-20 wt% pearlescent pigment.

5. An ink composition as in Claim 4, which is characterized by the fact that it contains 1-10 wt% pearlescent pigment.

6. An ink composition as in Claim 4 or 5, which is characterized by the fact that it contains 1-5 wt% pearlescent pigment.

7. An ink composition as in one of the preceding claims, which is characterized by the fact that it contains 75-90 wt% water.

8. An ink composition as in one of the preceding claims, which is characterized by the fact that the pearlescent pigment is in lamellar form, and the average particle diameter is less than 60  $\mu\text{m}$ .

9. An ink composition as in Claim 8, which is characterized by the fact that the particle diameter is less than 20  $\mu\text{m}$ .

10. An ink composition as in one of the preceding claims, which is characterized by the fact that the pearlescent pigment consists of mica that is coated with a metal oxide or of pearl essence.

11. An ink composition as in Claim 10, which is characterized by the fact that the metal oxide is  $\text{TiO}$ ,  $\text{TiO}_2$  or mixtures of these and/or  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  or mixtures of these.

12. An ink composition as in one of the preceding claims, which is characterized by the fact that the conventional additives include 0.5-10 wt% other pigments, 0.1-10 wt% water-soluble dyes, 0.5-20 wt% water-miscible organic solvents, 0.1-5 wt% dispersing agents, 0.5-20 wt% water-soluble binders, 0.1-2 wt% pH regulators, 0.01-0.5 wt% preservatives, 0.001-5 wt% surfactants and/or 0.1-10 wt% other auxiliary agents.

13. An ink composition as in one of the preceding claims, which is characterized by the fact that it additionally contains small inert mixing balls.

14. An ink composition as in Claim 13, which is characterized by the fact that the mixing balls have a diameter from 0.5 to 3 mm.

15. An ink composition as in Claim 13 or 14, which is characterized by the fact that the mixing balls have a diameter of 0.8 mm.

16. An ink composition as in one of Claims 13-15, which is characterized by the fact that 1-3 mixing balls are present in an ink cartridge.

17. An ink composition as in one of Claims 13-16, which is characterized by the fact that the mixing balls consist of zirconium dioxide or glass.

18. A method for preparation of the ink composition as in one of Claims 1-17, which is characterized by the fact that the components are mixed with each other in any order, optionally while heating them.

19. The use of an ink composition as in one of Claims 1-17 in devices in which the ink composition is applied to the writing material through narrow orifices, thin capillaries or small tubes.

20. The use as in Claim 19, which is characterized by the fact that the device is a fountain pen or a tube filler pen.



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### EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl <sup>5</sup> )
D,A	US-A-3 631 135 (PATRICK J. MCQUIRE) December 28, 1971 * Summary * * Claim 1 * ---	1	C09D11/16
P,A	DATABASE WPI Week 9324, Derwent Publications Ltd., London, GB; AN 93191709 & JP-A-5 117 569 (ZEBRA CO LTD) May 14, 1994 * Summary * ---	1,4-6, 10-12,19	
A	NL-A-8 900 296 (JOH. ENSCHEDE EN ZONEN GRAFISCHE INRICHTING B.V. TE HAARLEM) September 3, 1990 * Page 2, line 14 – page 3, line 13 * ----	1-6, 10-12	TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>5</sup> ) C98D
The present search report has been drawn up for all claims.			
Place of search THE HAGUE		Date of completion of the search February 28, 1994	Examiner Goerke, H
<b>CATEGORY OF CITED DOCUMENTS</b> X: Particularly relevant if taken alone. Y: Particularly relevant if combined with another document of the same category. A: Technological background. O: Non-written disclosure. P: Intermediate document. T: Theory or principle underlying the invention. E: Earlier patent document, but published on, or after the filing date. D: Document cited in the application. L: Document cited for other reasons. ..... &: Member of the same patent family, corresponding document.			